Title

Electro-Optic Modulators for R-FLICS based on a Self-Assembled Superlattice (SAS)

Seng-Tiong Ho

Department of Electrical and Computer Engineering
Northwestern University, Evanston, IL

Tobin J. Marks

Department of Chemistry and Materials Research Center

Northwestern University, Evanston, IL

Approved for public release, distribution unlimited

Collaborators

Yi-Guang Zhao

Seongsik Chang

Seng-Tiong Ho

ECE Department
Northwestern Univ.

Milko van der Boom

Joshua E. Malinsky

Tobin J. Marks

Chemistry Dept,
Northwestern Univ.

Wei-Kang Lu

Aiping Wu

Helen Lu

Lisa Wu

Wing Leon

Modulator Group,
Nanovation
Technologies

Susan Ermer

Rebecca Taylor

Lockheed Martin
Corp.

Gregory Zank

Dow Corning Corp.

Approved for public release, distribution unlimited

Outline

1. Introduction
2. Self-Assembled Superlattice (SAS) Materials
3. EO Modulator Device Design & Fabrication
4. Switching Voltage Measurements
5. Future Work

Approved for public release, distribution unlimited

Motivation

Next-Generation EO Modulators

- $LiNbO_3$ EO modulators with 10Gbit/sec data transfer rates are being used in current optical communication systems.

- Communication industries have identified 40 Gbit/sec as the requirement for next-generation EO modulators with below 5 volt to be compatible with integrated RF driving circuits.

- RF Photonics applications require switching voltage below 1 V.

- Current EO modulators are based on bulk-grown $LiNbO_3$ crystals and have reached close to their performance limits.
  → *Novel approaches* are required to realize the next-generation of EO modulators with bandwidths of 40 GHz and above.

Approved for public release, distribution unlimited

Our Approach

Materials

Organic: Self-Assembled Superlattices

Novel Device Design

Strongly Confined Thin-Film Waveguide

Approved for public release, distribution unlimited

Advantages

Materials

Polymer: Self-Assembled Superlattices

Molecular engineering of hyperpolarizability

-> *High EO coefficient ($r_{33} \geq$ 100pm/V)*

Low dielectric constant -> *Higher Bandwidth*

No Poling required -> *More stable, Simple design*

Tunable refractive index (n=1.5~1.75) -> *Better Confinement*

Novel Device Design

Strongly Confined Thin-Film Waveguide

Higher E-Field strength, better opto-rf field-overlap

-> *Lower switching voltage (< 5V)*

Reduced opto-rf Velocity-mismatch

-> *Higher Bandwidth (> 40GHz)*

Approved for public release, distribution unlimited

Goals of NWU's R-FLICS Program

Next-Generation SAS EO Modulators

I. Develop growth processes for intrinsically polar organic self-assembled superlattices (SAS)
   - Electric field poling unnecessary
   - Very large r_{33}, low ♏.

II. Develop capability to tune materials properties
   - r_{33}, n, ♏, loss

III. Develop fabrication methodologies to turn SAS materials into high-performance EO modulators.
   - Lithography, cladding, substrate generality

IV. Fabricate and test self-assembled electro-optic modulators.
   - Minimize V_{π}, loss

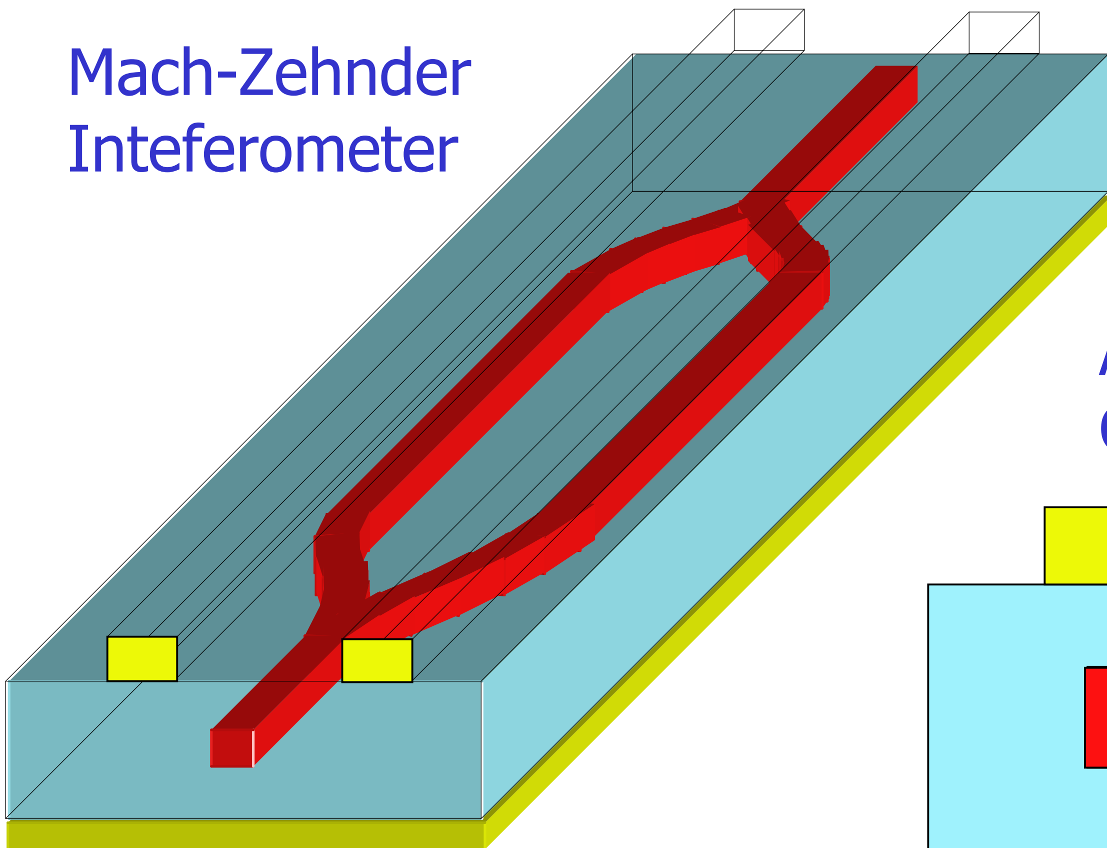
Approved for public release, distribution unlimited

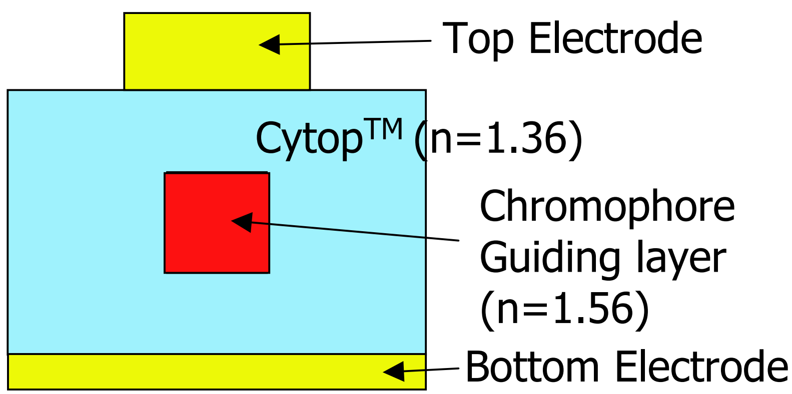
EO Modulators: Figures of Merit

	$LiNbO_3$	Poled EO Polymers	Self-Assembled Superlattice
EO coefficient (pm/V)	31	10-75	30-200
Dielectric constant, ε	28	4	6
Refractive Index n	2.2	1.6	1.6
n^3r (pm/V)	248	150	120-820
n^3r/ε	8.7	40	20-820

Approved for public release, distribution unlimited

Optical Waveguide Structure

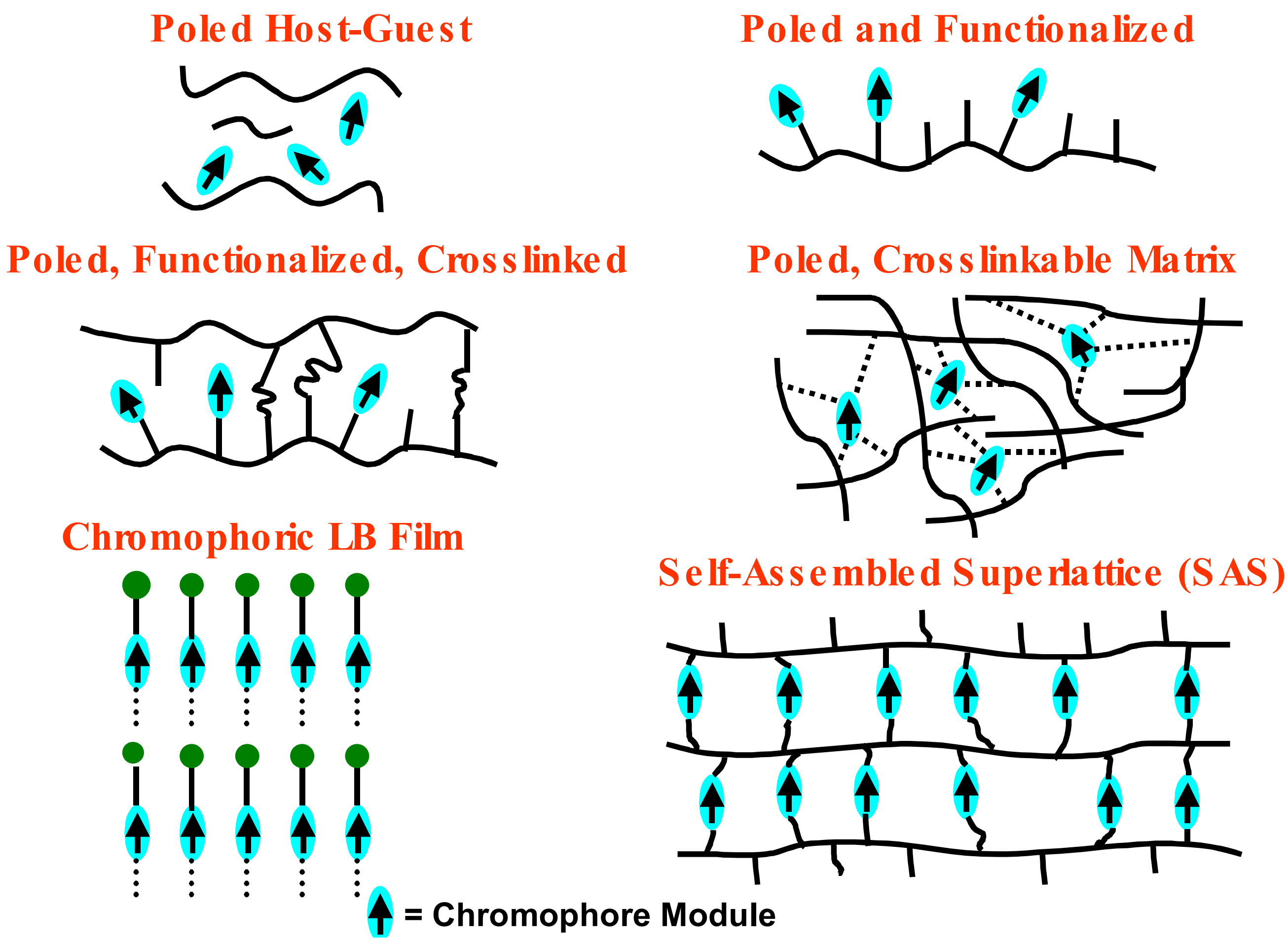




Northwestern University

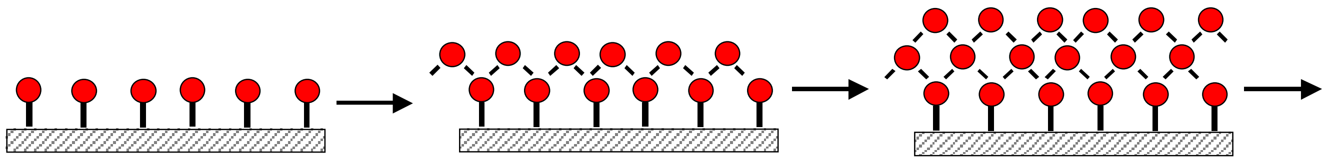
Approved for public release, distribution unlimited

Design Motifs for Molecular/Polymer Electro-Optic Materials

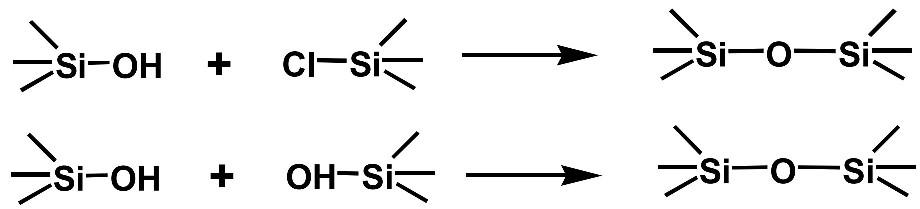


Approved for public release, distribution unlimited

Materials Construction via Layer-by-Layer Siloxane Self-Assembly



Condensation Chemistry



Characteristics

Å-Precise Self-Limiting Build-Up of Cross-Linked Multilayers
Robust, Conformal, Smooth, Adherent, Pin Hole-Free
Applicable to Many Molecular Building Blocks

Characterization

SPM, X-Ray Reflectivity, Standing Wave X-Ray, Ellipsometry, Optical Spectroscopy, Cyclic Voltammetry, Advancing Contact Angle, TGA, SHG Response
Electroluminescence

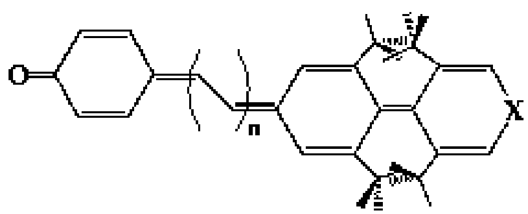
Approved for public release, distribution unlimited

Electronic Structure Theory in Materials Development

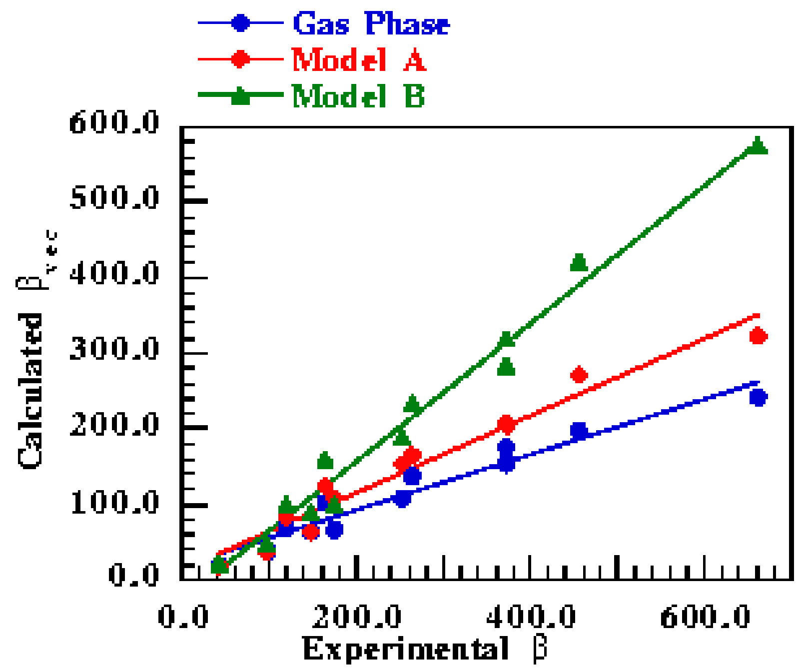
Correction Vector/Sum-Over-States ZINDO Calculations

Attractions

- Target New Molecular Architectures For Synthesis
- Test New Response Mechanisms
- Understand Mechanisms, Frequency Dependence



$\mu\beta(0.65\ eV) = 200.000 \times 10^{-48}$ esu



Challenges

- Environmnetal Effects
- Metal-Organic Structures
- Open Shell Molecules, Excited States
- Luminescent Electron-Hole Recombination

Ratner, Fragala, Di Bella

Northwestern University

Approved for public release, distribution unlimited

What are Self-Assembled Electro-Optic Materials?

- Environmentally Stable, Adherent Thin Films
- Grown from Designed Building Blocks
- Manufacturable by Automated Dipping Techniques
- Northwestern Patent Coverage

Attraction for E-O Modulators

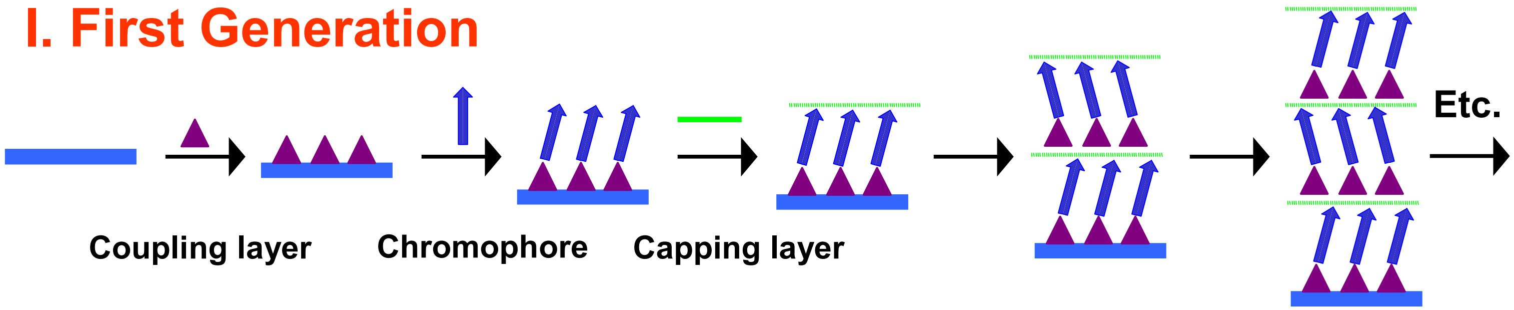
- Intrinsically Polar
  Electric Field Poling Unnecessary
- Large E-O Coefficients Possible → Low Operating Voltages
  r_{33} = 30 - 500 pm/V
- Grown on Range of Substrates
  SiO_2, GaAs, ITO, Plastics, Spin-on-Glass
- Broad Tunable Transparency Window

Approved for public release, distribution unlimited

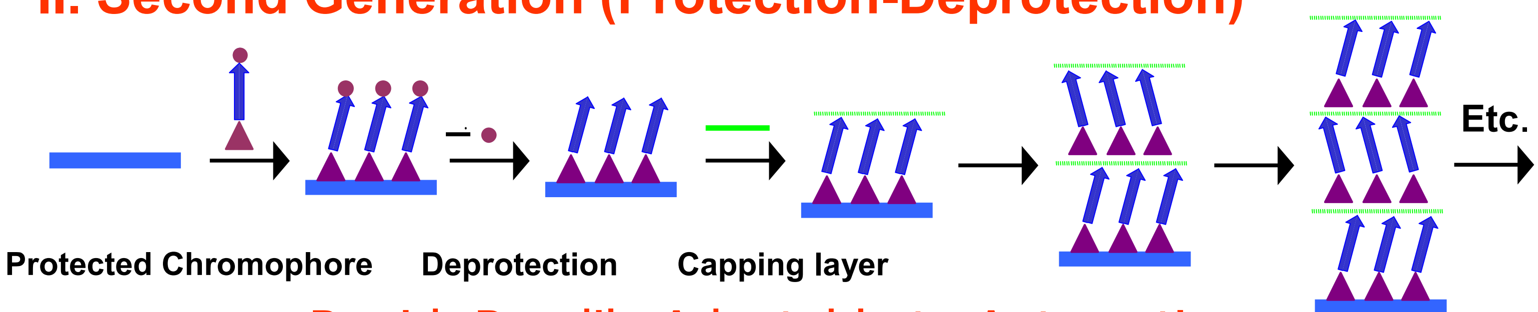
STRUCTURES AND MULTILAYER GROWTH BY MOLECULAR SELF-ASSEMBLY

- Programmed Polar Microstructure
- Tailored Building Blocks
- Compatible with Soft Lithography
- n^3r/ε = 20-140 pm/V
- Synthetic Scope, Fidelity, Scalability
- Tune λ, β, r
- Templated Growth, Device Integration
- Microstructure, Loss

I. First Generation



II. Second Generation (Protection-Deprotection)



Rapid. Readily Adaptable to Automation

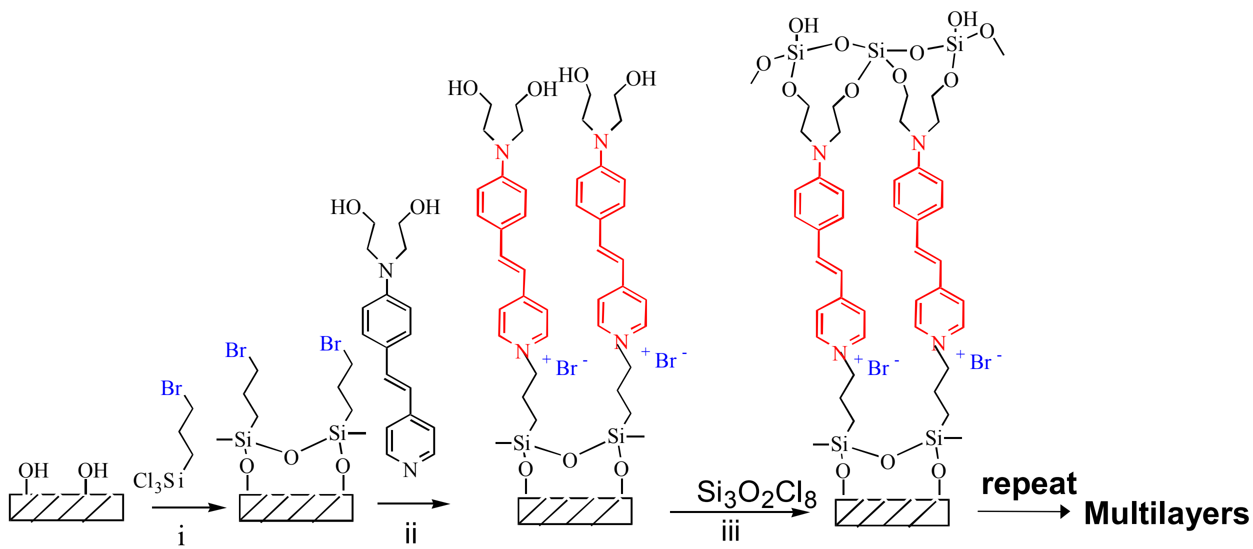
Robust, Adherent, Smooth, Structurally, Regular Siloxane Networks

Northwestern University

Approved for public release, distribution unlimited

Construction of Chromophoric Multilayers by Molecular Layer Epitaxy

First Generation Self-Assembly

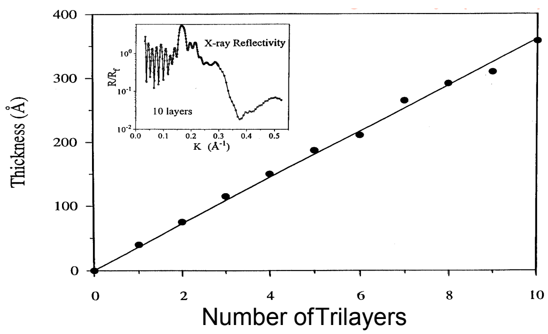


1. Rapid Topotactic Multilayer Growth
2. Intrinsically Acentric (No Poling Required)
3. Very High Structural Regularity
4. Very Large $\chi^{(2)}$ Response

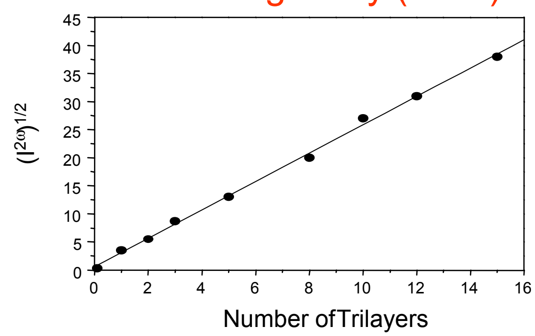
Approved for public release, distribution unlimited

First Generation Self-Assembled Electro-Optic Materials

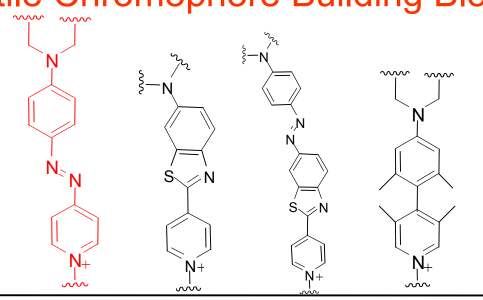
Microstructural Regularity (XRR)



Polar Regularity (SHG)

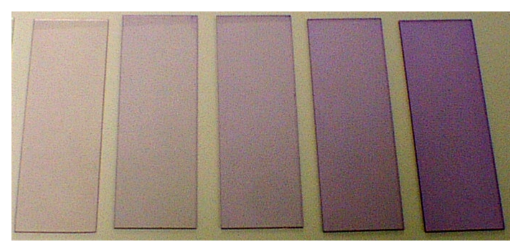


Versatile Chromophore Building Blocks



β (0.65 eV) calcd. (10^{-30} cm^5 esu^{-1})	178	360	1244	>10,000
λ_{max} calcd. (nm)	572	498	510	610
Film r_{33}, ω_o=1064 nm (pm/V)	56	125	180	>2000
Generation Method	1,2	1	2	

Samples of Self-Assembled Films

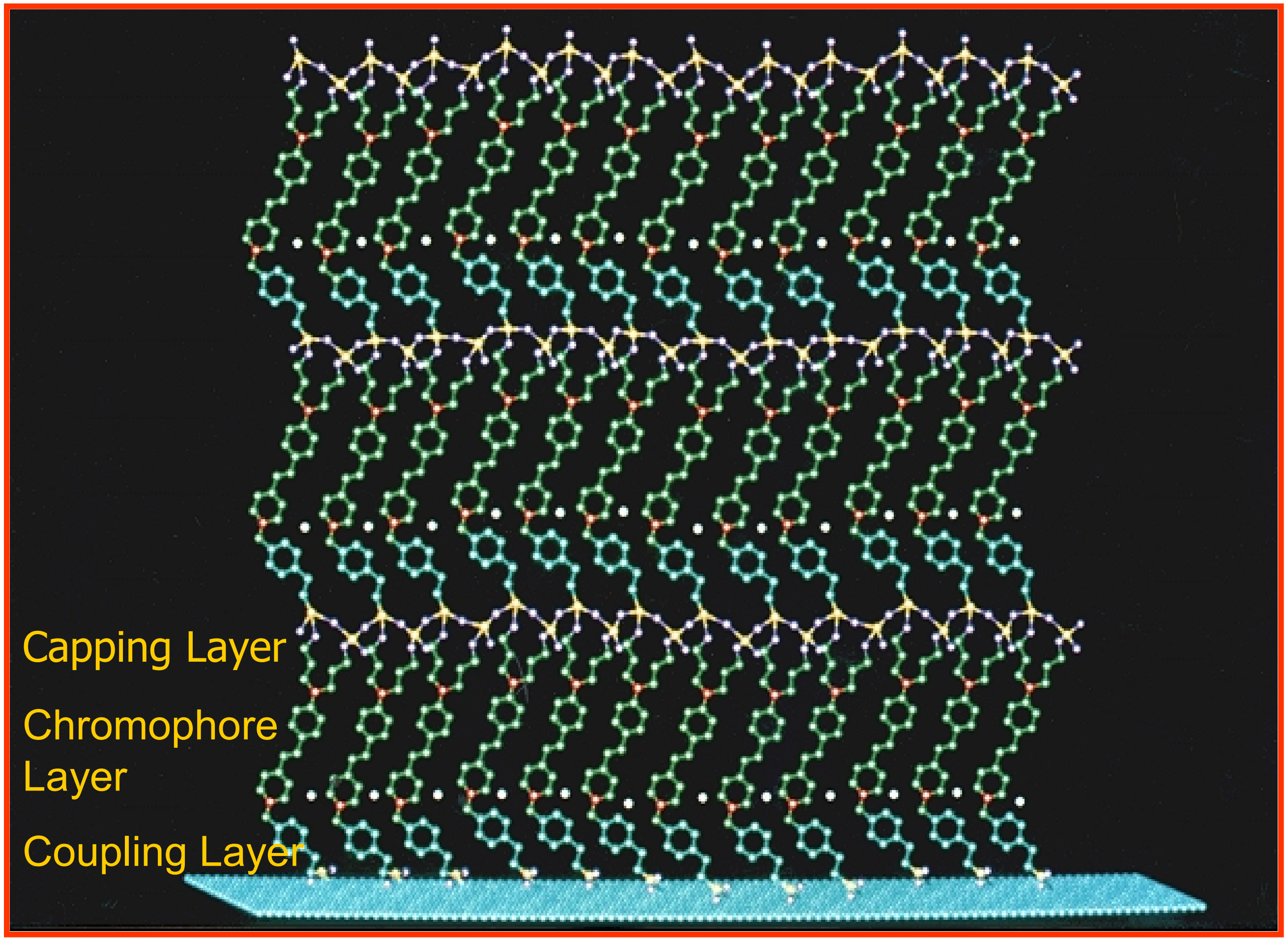


1 2 3 4 5

Number of Trilayers

Approved for public release, distribution unlimited

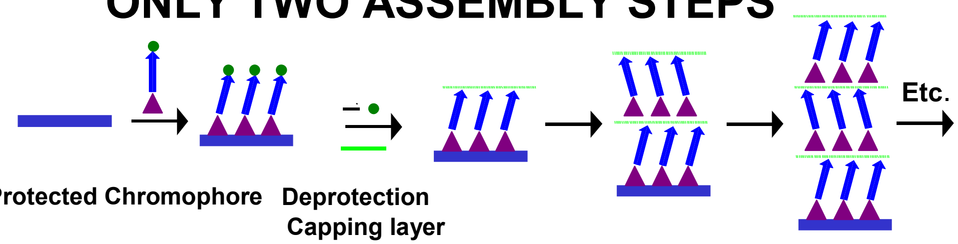
Molecular Modeling of SAS

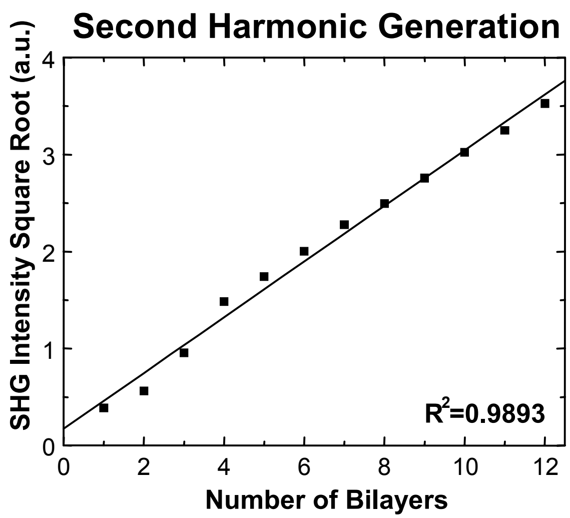


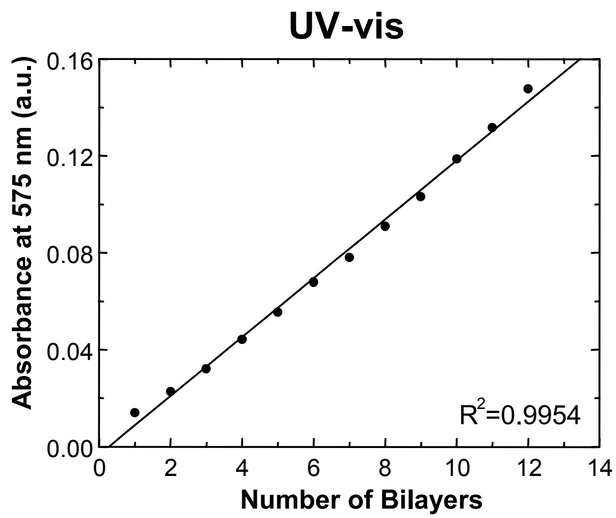
Approved for public release, distribution unlimited

Second Generation: Combining the Deprotection and the Capping Step

ONLY TWO ASSEMBLY STEPS

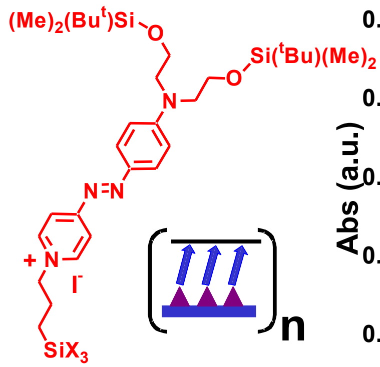


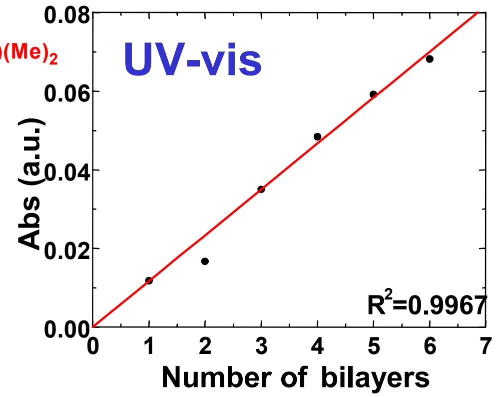


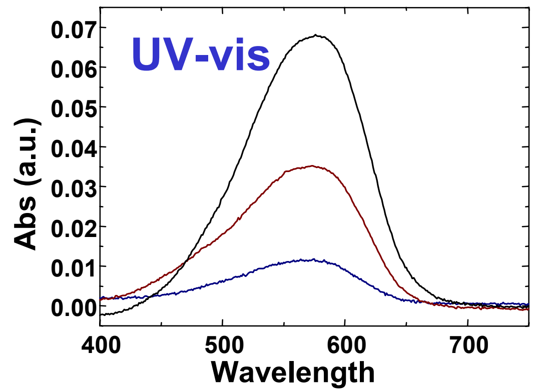


Approved for public release, distribution unlimited

2nd Generation Self-Assembly (Protection-Deprotection)







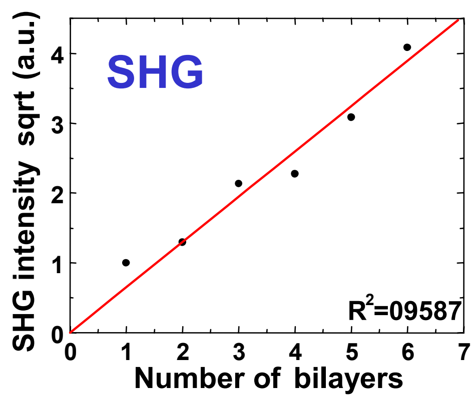
Reactive SiX_3 (X = Cl, I) for rapid assembly

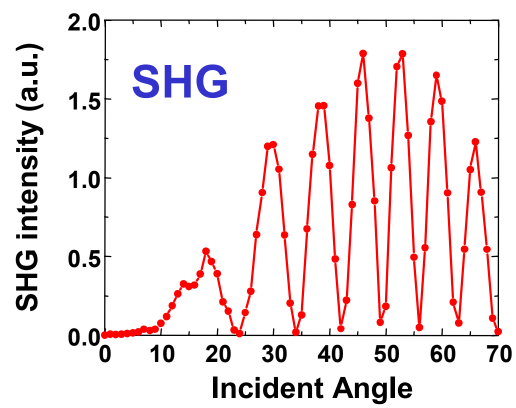
Reaction Time

Chromophore : 10 min

Deprotection : 4 min

Capping Layer: 30 min

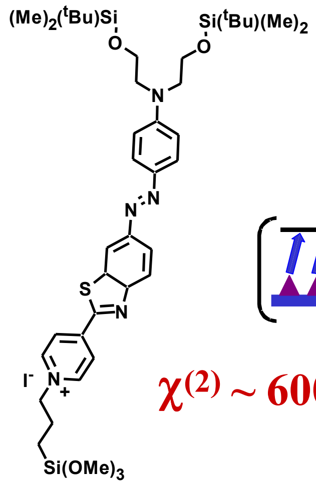


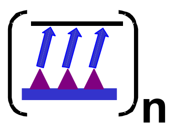


Northwestern University

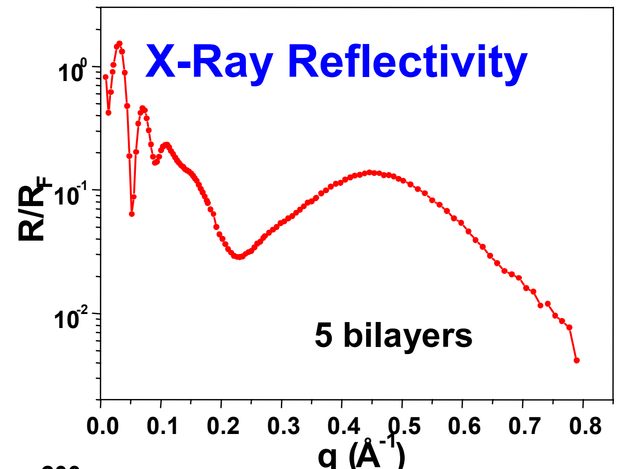
Approved for public release, distribution unlimited

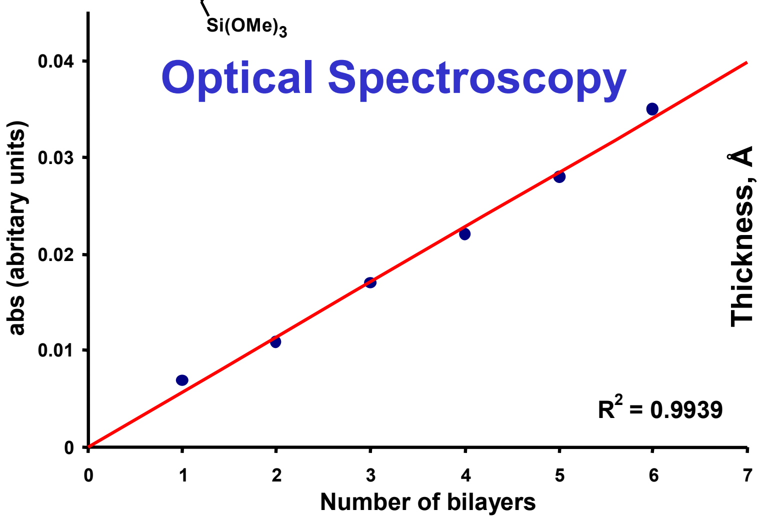
2^{nd} Generation Self-Assembly: Results II

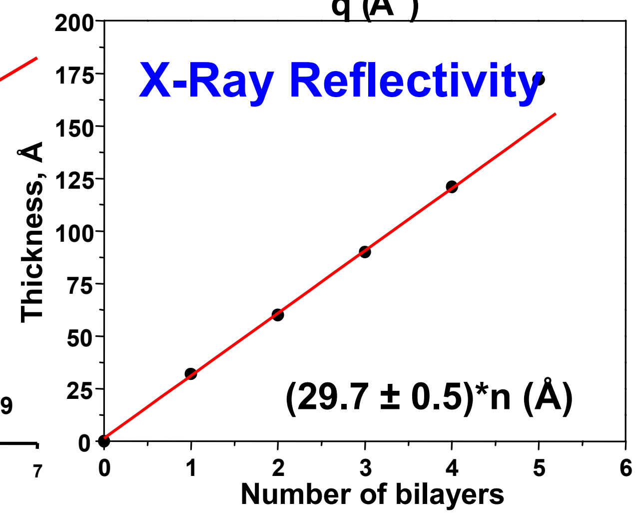




$\chi^{(2)} \sim 600$ pm/V



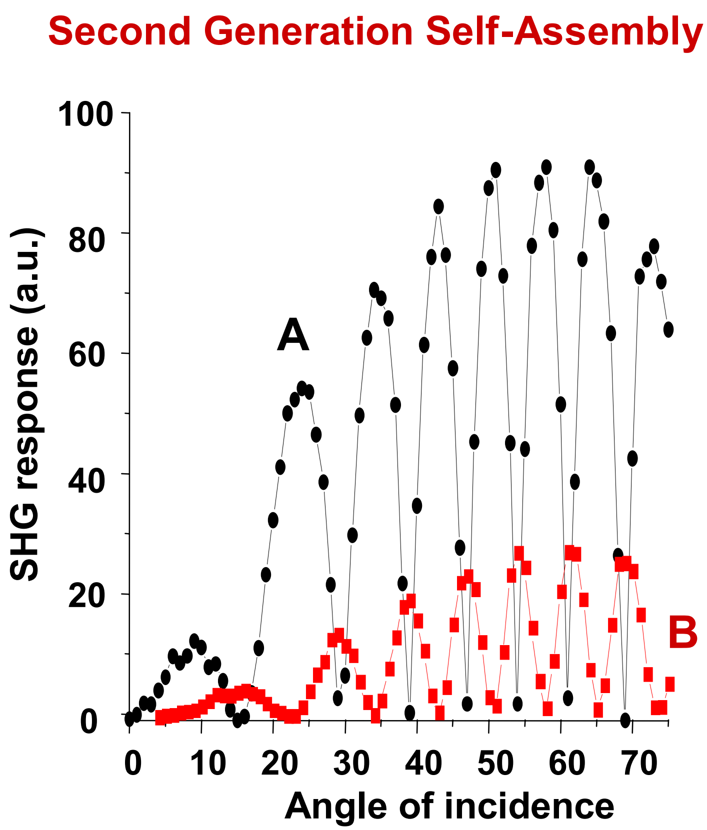


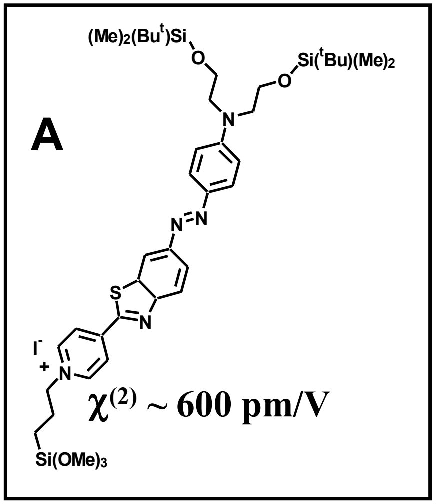


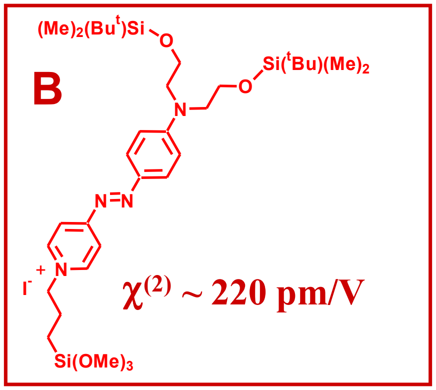
Northwestern University

Approved for public release, distribution unlimited

Comparison of NLO Properties of Thin Films



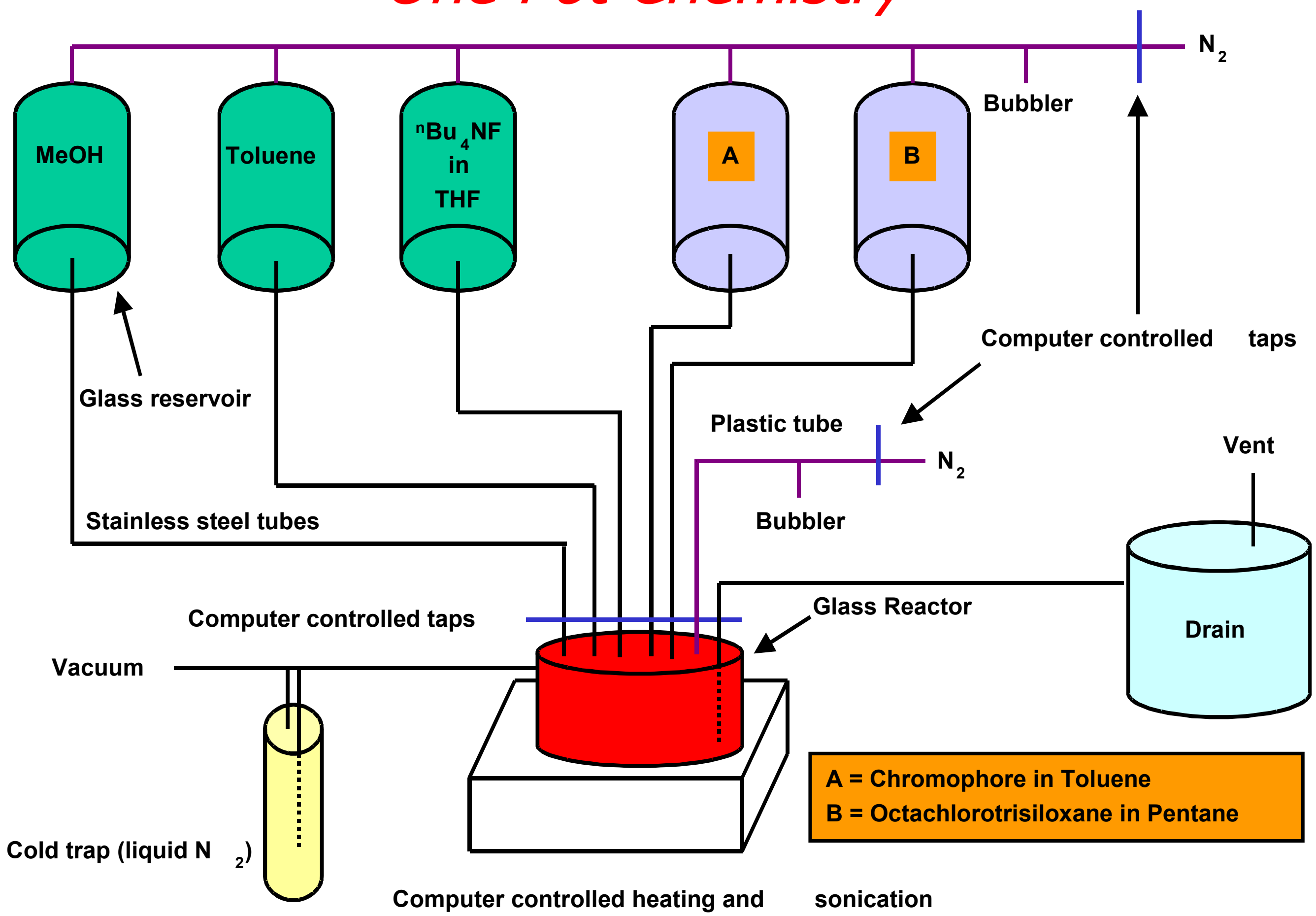




Approved for public release, distribution unlimited

2nd Generation Self-Assembly: Growth Method

"One Pot Chemistry"

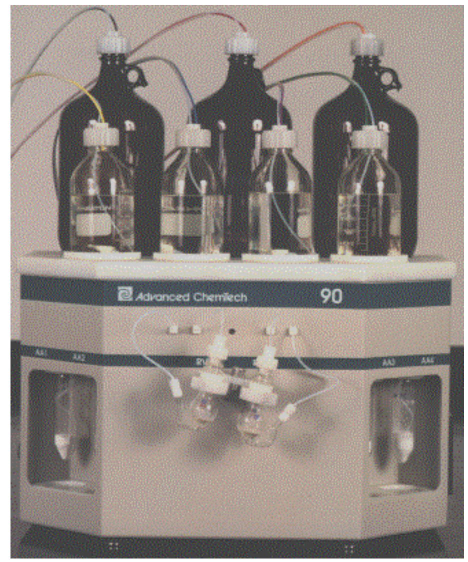


Approved for public release, distribution unlimited

Automation Tools for Self-Assembly

MODIFIED BIO SLIDE STAINER/DIPPER

MODIFIED SOLID PHASE PEPTIDE SYNTHESIZER

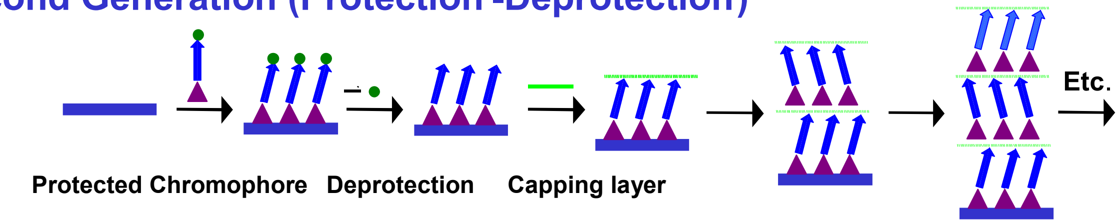


ALLOW PROGRAMMED LAYER-BY-LAYER FABRICATION

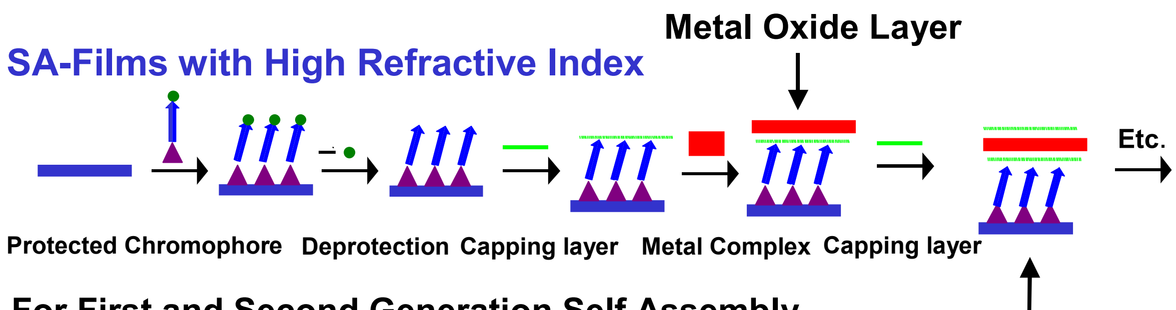
Approved for public release, distribution unlimited

Development of Growth Process

Second Generation (Protection -Deprotection)



SA-Films with High Refractive Index

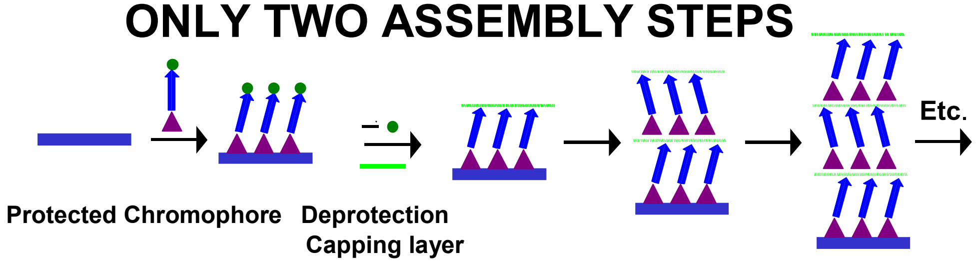


For First and Second Generation Self-Assembly

'BIFUNCTIONAL HYBRID STRUCTURE'

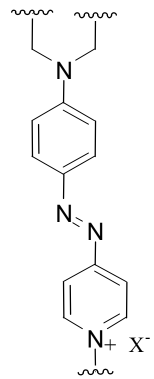
Second Generation: Combining the Deprotection and the Capping Step

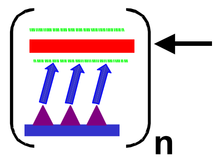
ONLY TWO ASSEMBLY STEPS



Approved for public release, distribution unlimited

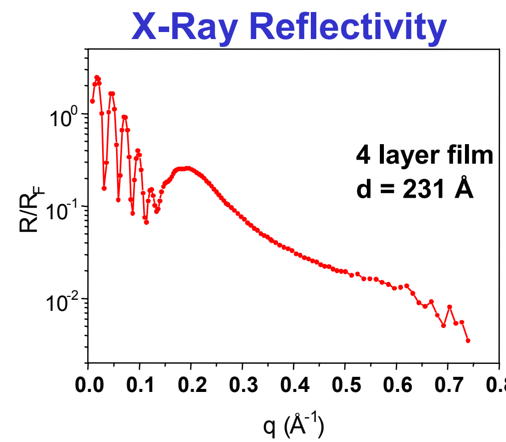
2nd Generation Self-Assembly with High Refractive Index SA Films



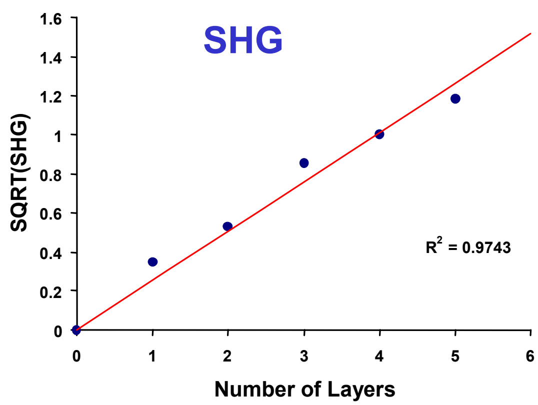


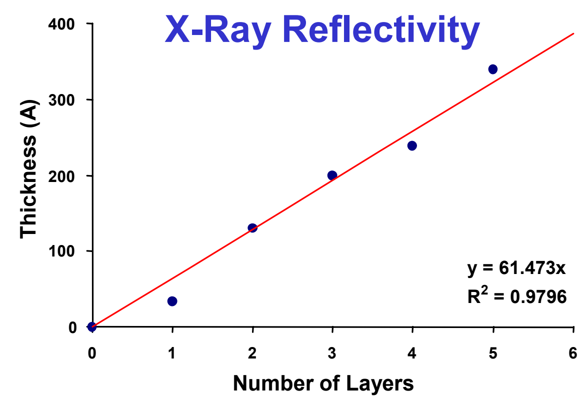
Gallium Oxide

Gallium observed by XRR, XPS, and ICP



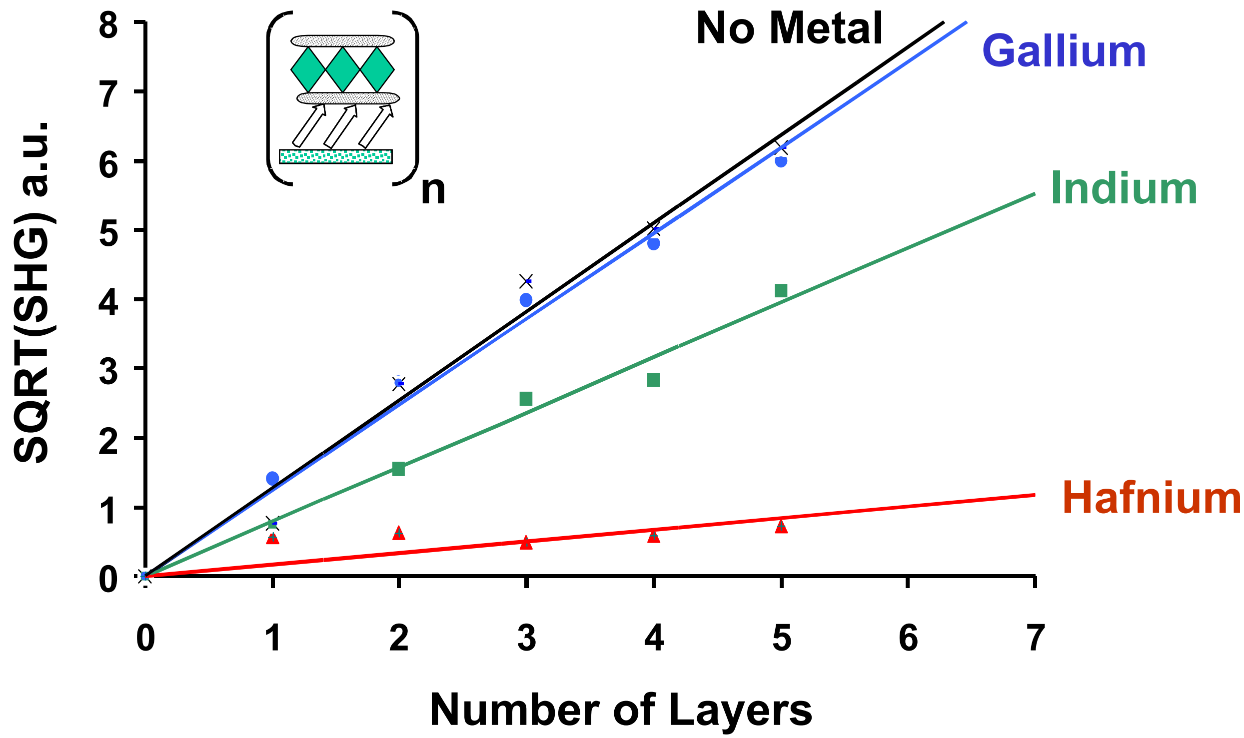
Gallium oxide formation in 30 min at r. t. from commercially available precursor





Approved for public release, distribution unlimited

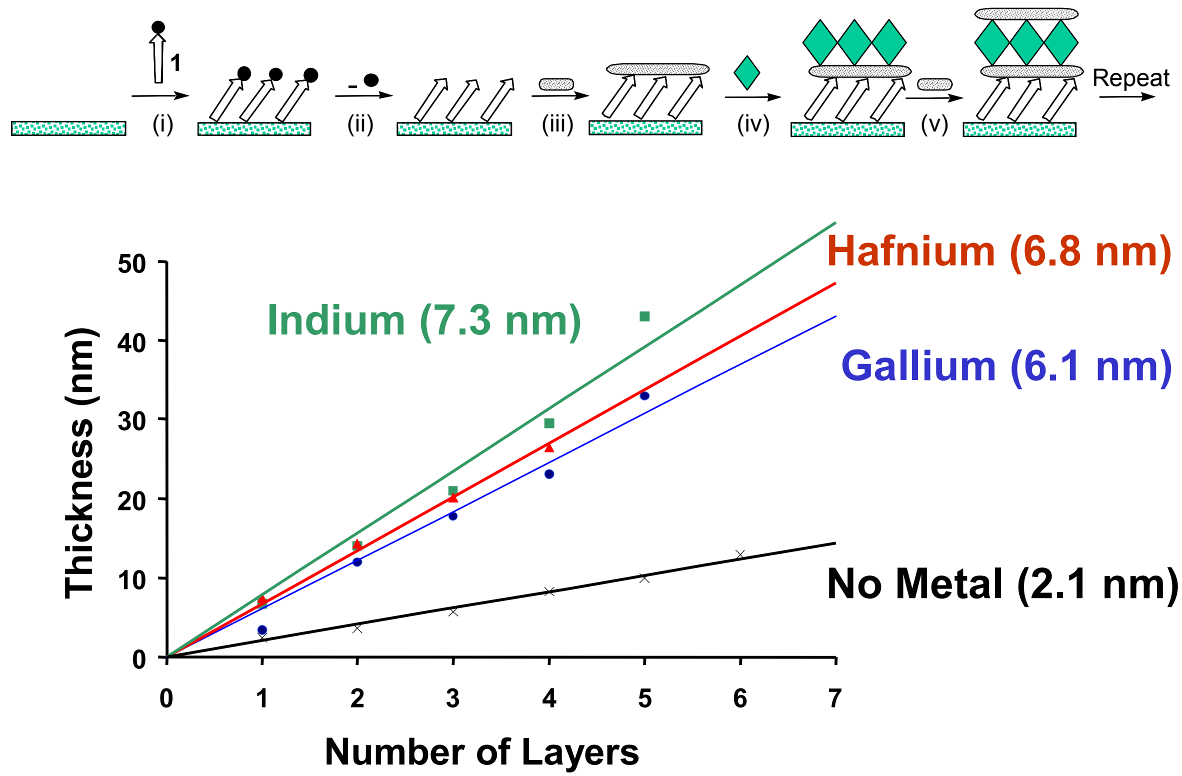
Second Harmonic Generation @1064nm



Northwestern University

Approved for public release, distribution unlimited

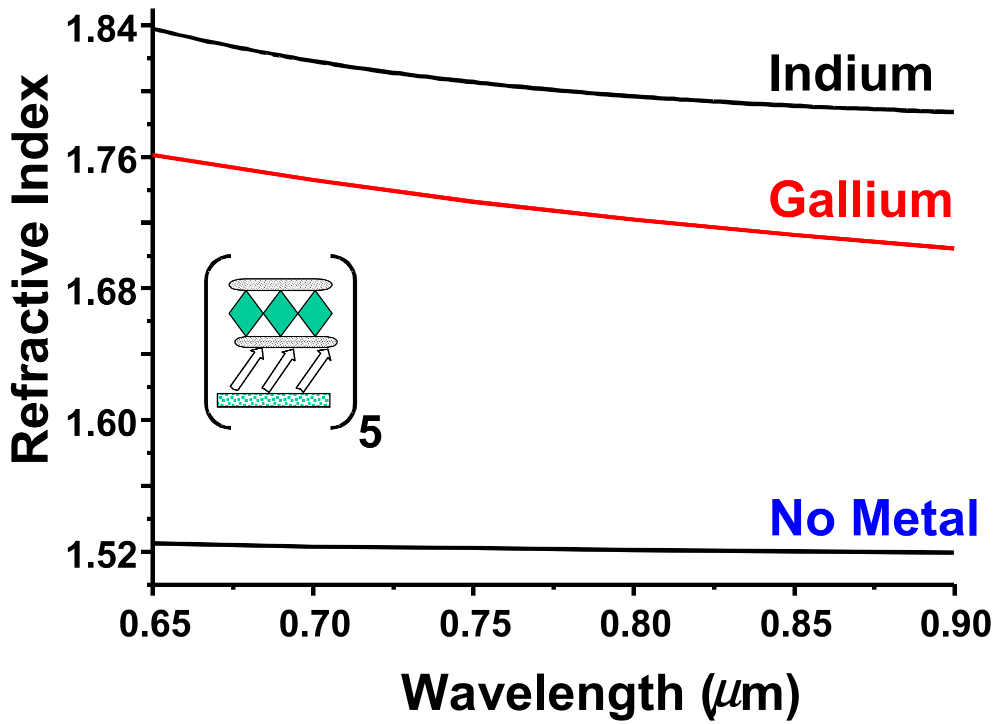
X-Ray Reflectivity (XRR)



Approved for public release, distribution unlimited

Index of Refraction Measurements

Of SASs with Various Metal-Oxides

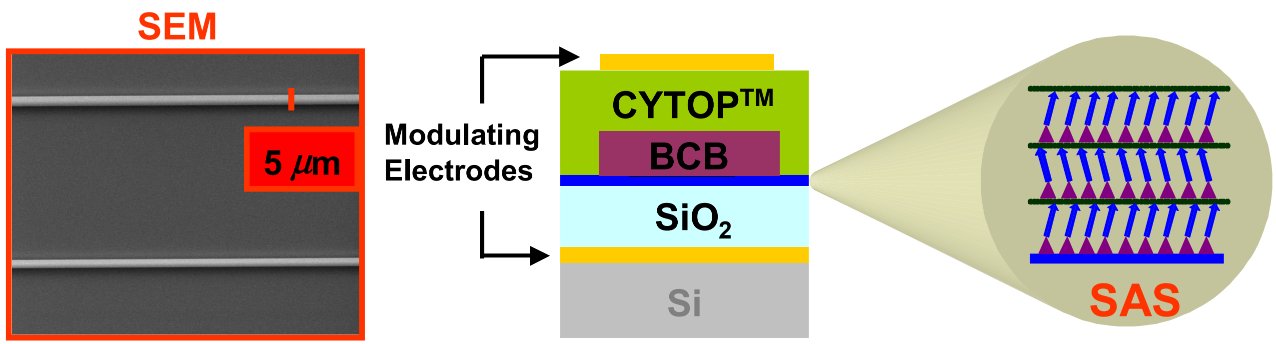


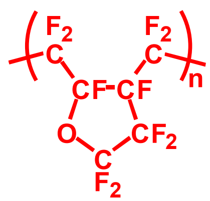
Northwestern University

Approved for public release, distribution unlimited

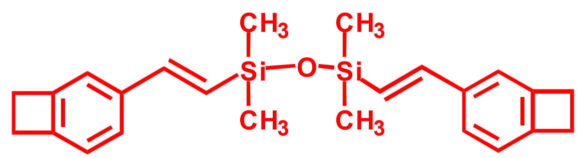
ELECTRO-OPTIC MATERIALS SYNTHESIS BY SELF-ASSEMBLY

- Programmed Polar Microstructure
- Tailored Building Blocks
- Compatible with Soft Lithography
- n^3r/ε = 20-140 pm/V
- Synthetic Scope, Scalability
- Tune λ, β, r
- Templated Growth, Device Integration
- Microstructure, Loss





CYTOP™



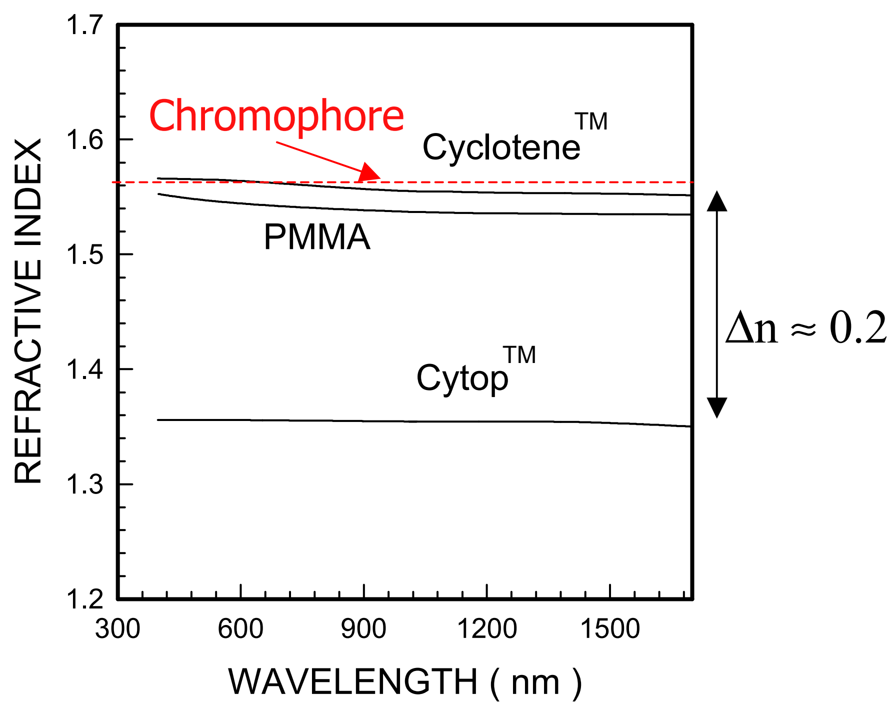
CYCLOTENE™ (BCB)

First Self-Assembled EO Modulator

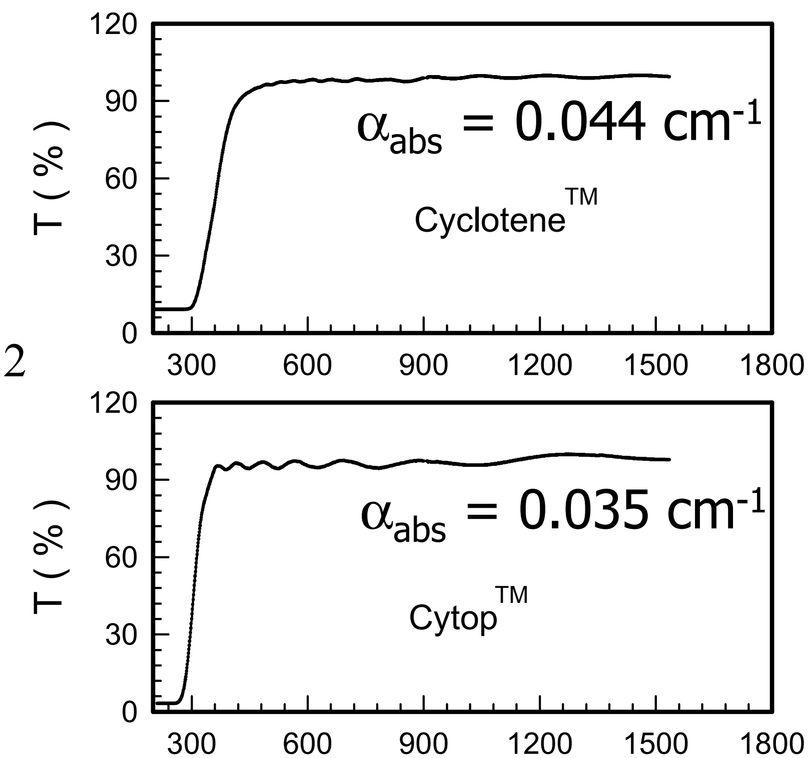
Approved for public release, distribution unlimited

Optical Properties of Polymers

Index of Refraction

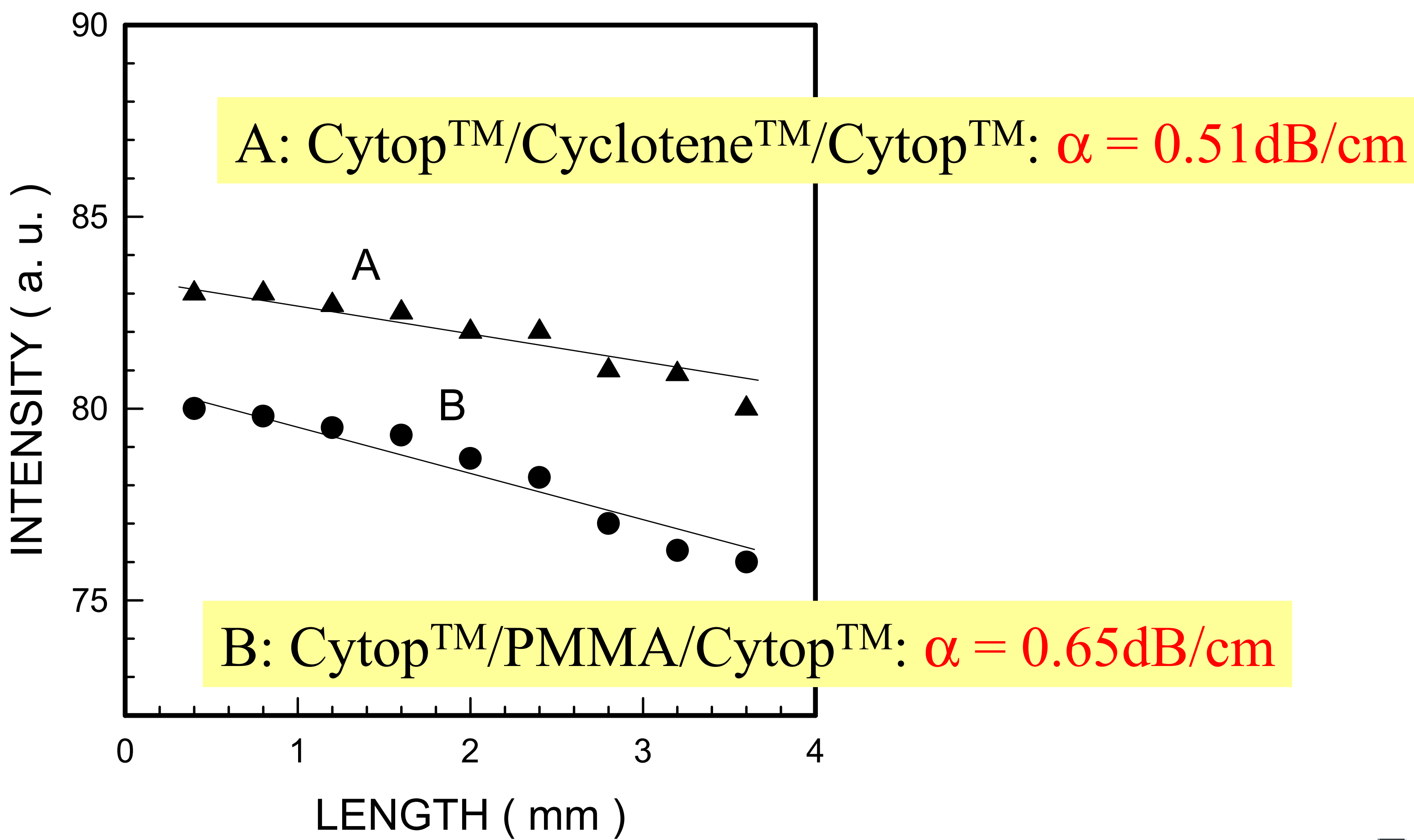


Transmission Spectra



Approved for public release, distribution unlimited

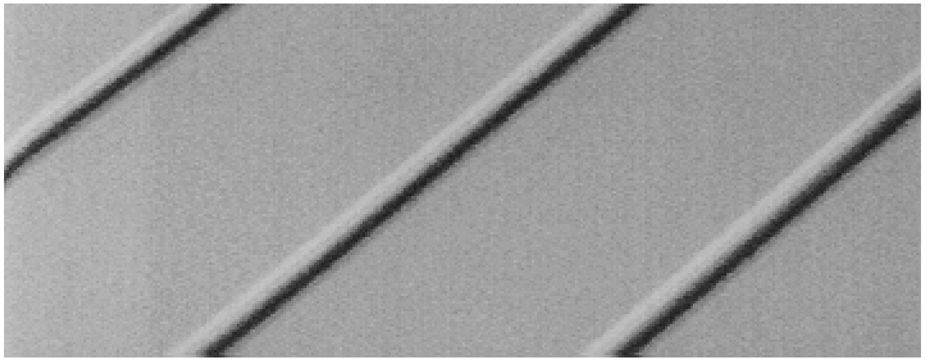
Propagation Loss Measurements

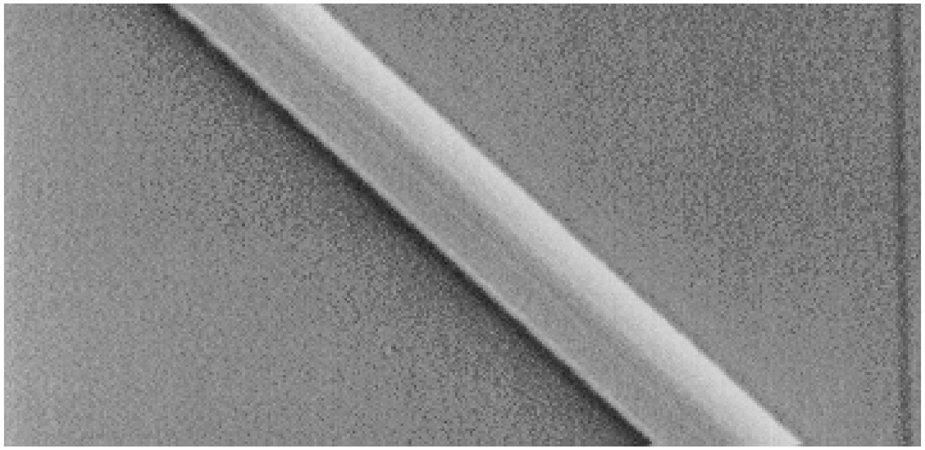


Northwestern University

Approved for public release, distribution unlimited

SEM Images of Waveguides

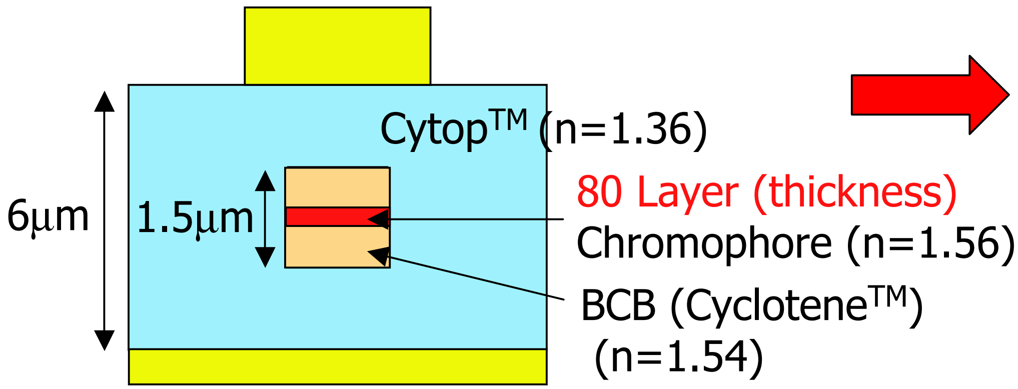


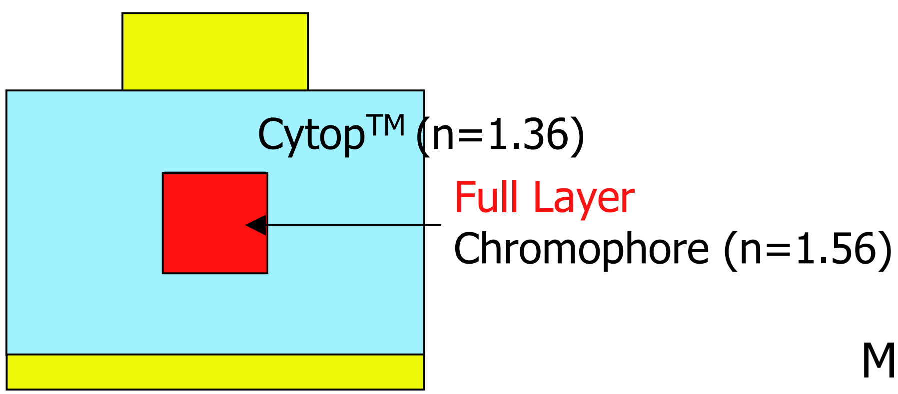


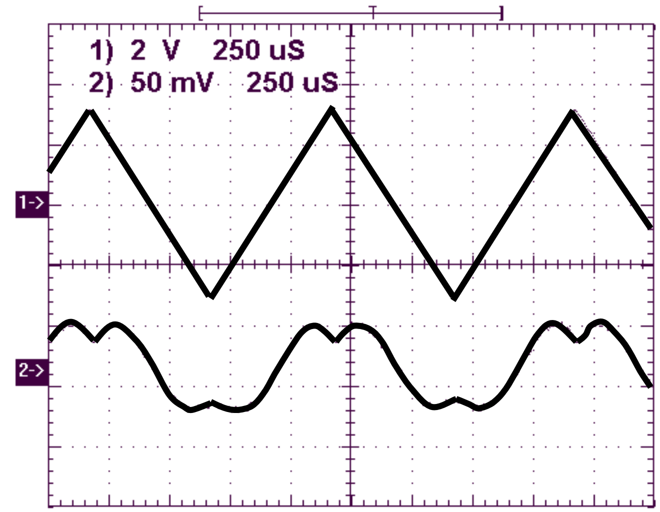
Northwestern University

Approved for public release, distribution unlimited

Current Prototype Modulator







$V_{\pi} \cdot L = 88$ V·cm

$R_{33} \sim 22$ pm/V

Projection (1st Gen)

$V_{\pi} \cdot L \leq 5$ V·cm

MZI + Push-Pull

Northwestern University

Approved for public release, distribution unlimited

Device Optimization

Index Tuning of SAS

Molecular engineering gives extra degrees of freedom in varying chromophore layer index of refraction

Goal of Optimization:
1. Lower Switching Voltage

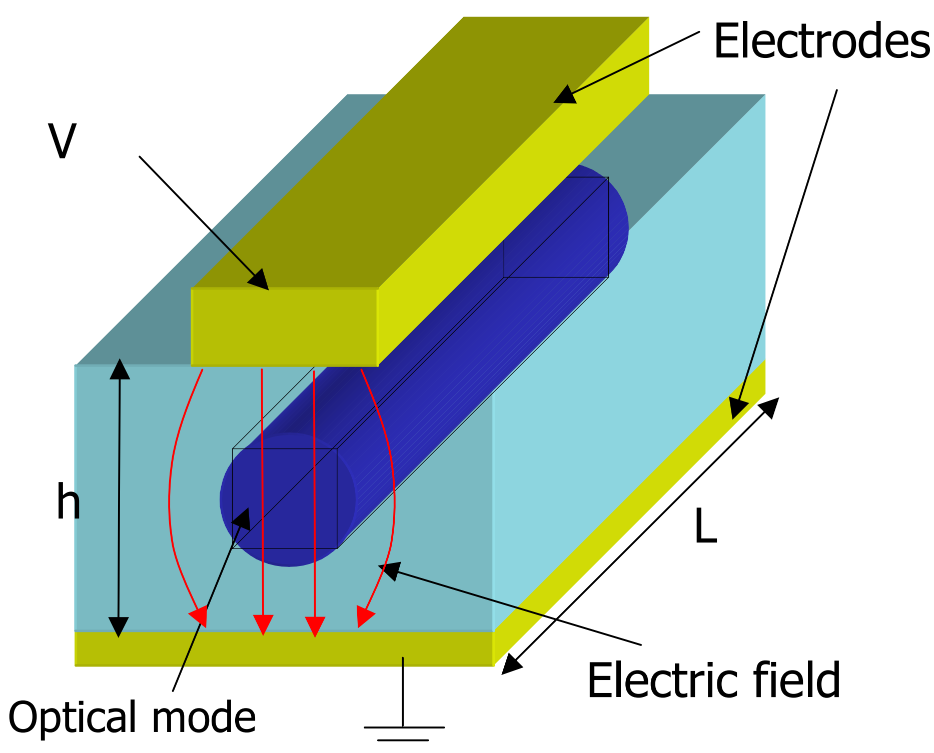
2. Higher Modulation Bandwidth

3. Better Confinement of Light

Approved for public release, distribution unlimited

Switching Voltage (V_π)

$$V_\pi \cdot L = \frac{\lambda h}{2 n_{eff-opt}{}^3 r \Gamma_e \Gamma_o}$$



$n_{eff-opt}$:effective optical index

r :EO coefficient

Γ_o :optical overlap factor

Γ_e :electrical overlap factor

Approved for public release, distribution unlimited

Modulation Bandwidth

$$H(f)=e^{-\frac{\alpha L}{2}}\left[\frac{\sinh^2(\frac{\alpha L}{2})+\sinh^2(\frac{\xi L}{2})}{\left(\frac{\alpha L}{2}\right)^2+\left(\frac{\xi L}{2}\right)^2}\right]^{\frac{1}{2}}$$

$\xi = 2\pi f \dfrac{n_{RF}-n_{opt}}{c}$:Velocity mismatch between RF and optical waves

➡ Determines "Walk-off bandwidth"

α_{RF} : RF attenuation coefficient $\propto \sqrt{f}$

➡ Induces RF power loss along the electrodes

Approved for public release, distribution unlimited

How Higher Index Improves the Performance

1. Lower switching voltage

- $V_\pi \propto 1/n^3 r$
- Higher n -> Smaller optical mode size
  -> Reduced Electrode separation
  -> Higher E-field strength

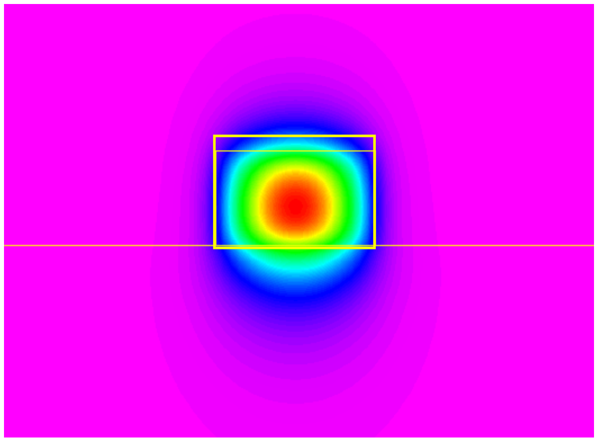
2. Fewer active layer needed

   by reduced optical mode size

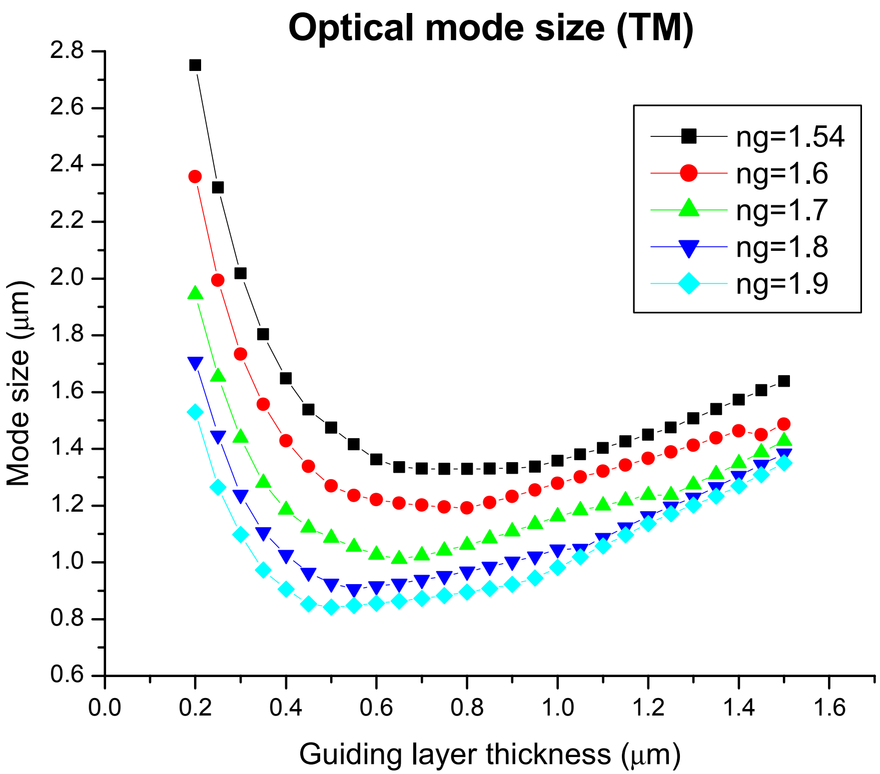
Approved for public release, distribution unlimited

Optical Mode Calculation

Beam Propagation Method:
Mode size calculation

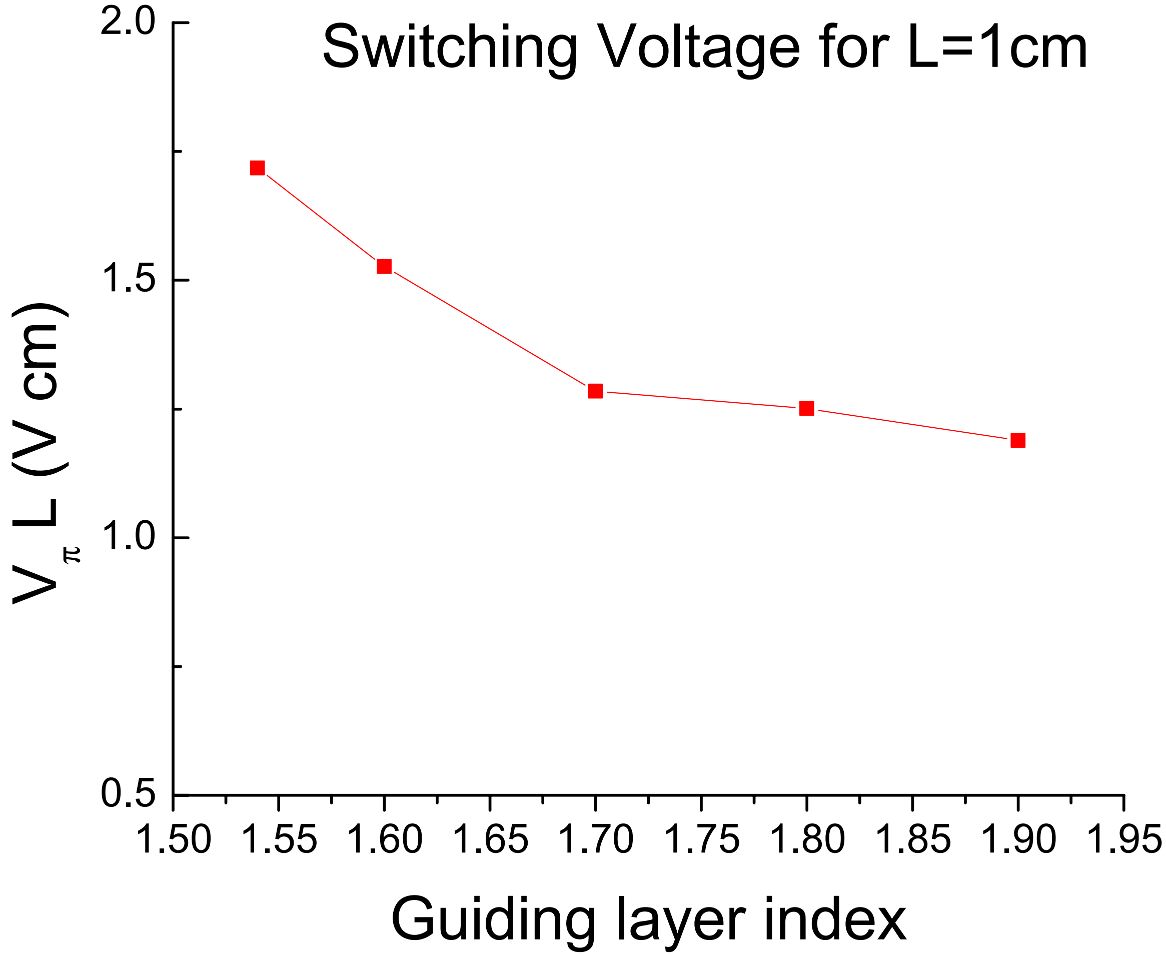


Effective Index Method:
Optical Ovelap factor (Γ_0)



Approved for public release, distribution unlimited

Switching Voltage vs. Guiding Layer Index



Assumption:

R_{33} = 60pm/V

h = 3 μm

Electrode separation

Approved for public release, distribution unlimited

RF Simulation I

Quasi-static Finite Element Methods:

→ Provides C & C_0

C: Capacitance with materials present
C_0: Capacitance with air

(1) Velocity mismatch: effective RF index

$$n_{eff-opt} = \sqrt{\frac{C}{C_0}}$$

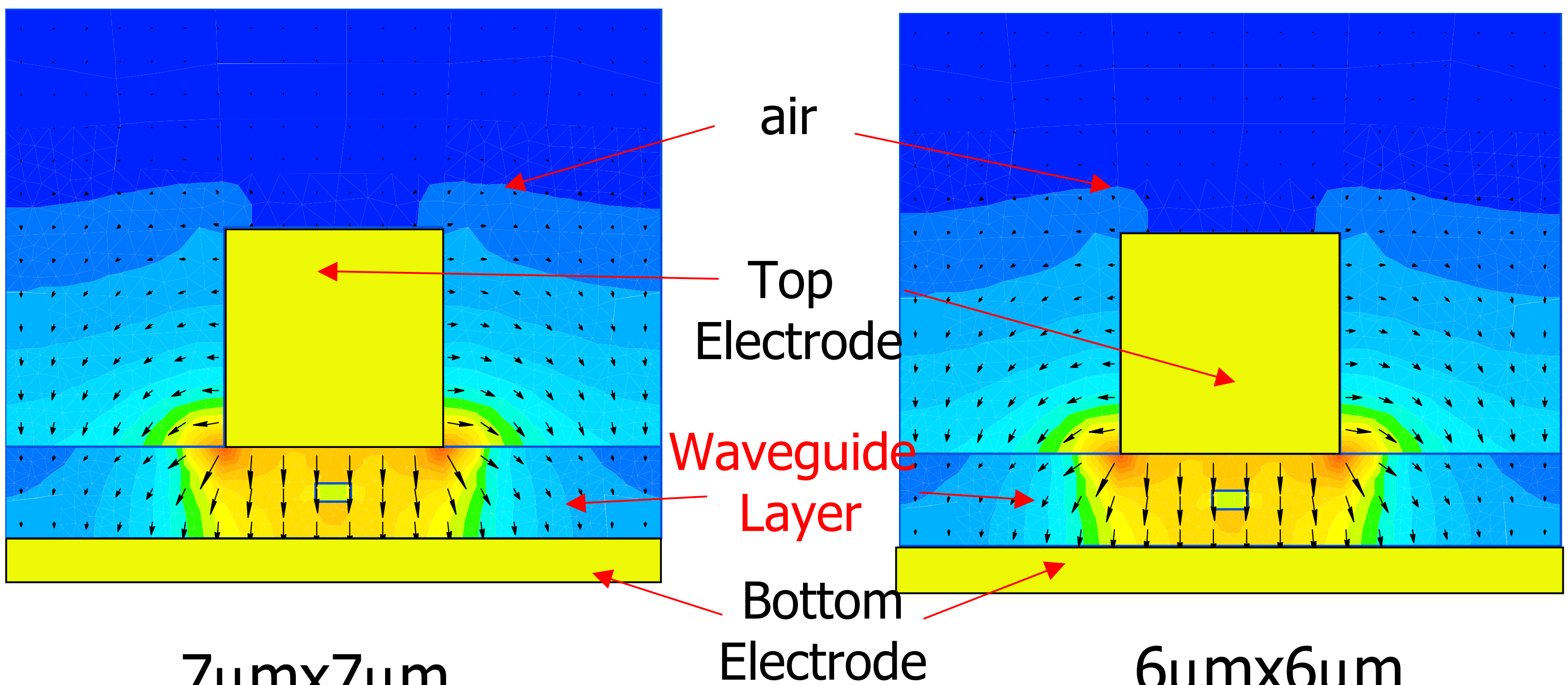
(2) Characteristic impedance:

$$Z = \frac{1}{c\sqrt{CC_0}}$$

Approved for public release, distribution unlimited

RF Simulation II

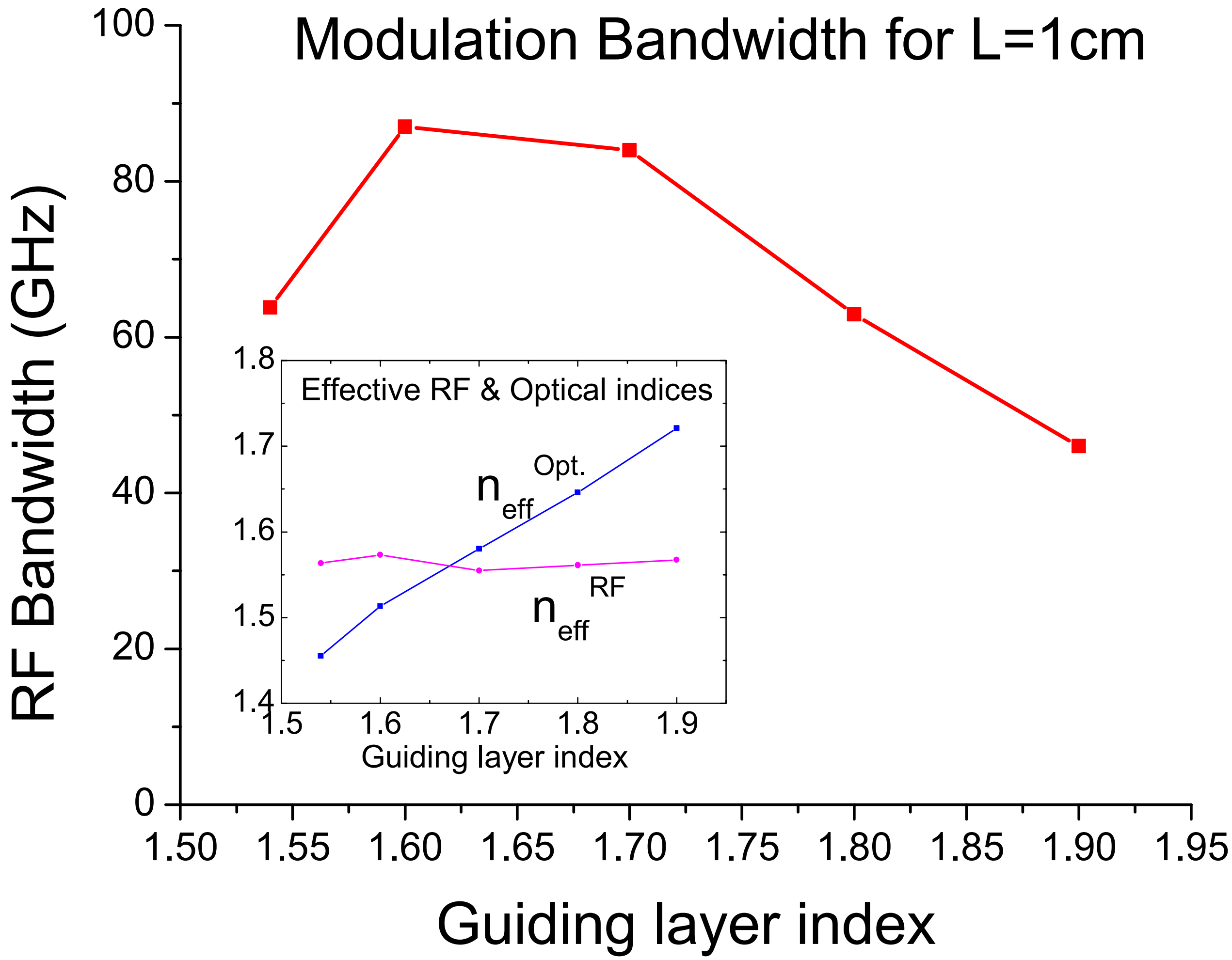
n_{SAS} = 1.54 $\qquad$ n_{SAS} = 1.7



7µmx7µm		6µmx6µm
42.7 ohm	:Impedance:	41.5 ohm
1.56	:RF index:	1.55

Approved for public release, distribution unlimited

RF Bandwidth vs. Guiding Layer Index



Approved for public release, distribution unlimited

Most Significant Accomplishments

SAS Materials Development

- Highly efficient protection-deprotection growth technique demonstrated
  - ♍$^{(2)}$ 🕔 220pm/V, r_{33} 🕔 80pm/V
- Automated growth apparatus implemented for SAS structures
- Metal oxide layer incorporation demonstrated for index tuning

Device Development

- All polymer waveguides demonstrated with good transparencies from 350-1650nm
  - Cytop™/Cyclotene™/Cytop™: ♋=0.5 dB/cm
- First SAS electro-optic modulators fabricated and tested
  - Simple design, Vπ-L=88 V-cm
  - Route to low Vπ clear: Thicker films, longer devices, advanced chromophores

Approved for public release, distribution unlimited

Future Efforts

Y1 Streamline growth techniques
Tune refractive index
All-polymer waveguide
Fabricate first SAS modulator

Y2 Routine automated assembly
Grow, characterize thick active SAS structures
Design, routinely fabricate, characterize modulators

Y3 Incorporate “super-chromophores” in SAS structures
Automated index tuning
Design, routinely fabricate, characterize modulators

Y4 Implement soft lithography to template SAS growth
Demonstrate efficiently fabricated SAS modulators with $V\pi<1V$
Test modulators in various environments

Approved for public release, distribution unlimited

Conclusions

1. Switching voltage is measured for the first time from the SAS-organic modulator:

   $V_{\pi} \cdot L = 88$ V·cm for 80 Layer

   -> projected to be $V_{\pi} \cdot L \leq 5$ V·cm for a device with fully grown chromophore layer

2. Device optimization simulation performed using index tuning of SAS:
   Higher index gives lower switching voltage and Fewer SAS layer needed.

Approved for public release, distribution unlimited